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Anion effects on the cyclobis(paraquat-*p*-phenylene) host

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ELECTRONIC SUPPLEMENTARY INFORMATION

(22 Pages)

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EXPERIMENTAL DETAILS

Materials. All reactions were carried out under an atmosphere of anhydrous N₂ unless otherwise stated. DMF was dried by allowing it to stand over molecular sieves (4 Å) for at least 3 days prior to use. All used reagents were standard grade and used as received, except 2-{4-(2-(2-methoxyethoxy)-ethylthio)-5-ethylthio-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole,^{S1} bis(pyrrolo[3,4-*d*])tetrathiafulvalen,^{S2} 1,5-dimethoxynaphthalene^{S3} morpholinium•TRISPHAT,^{S4} and cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) CBPQT•4PF₆,^{S5} which were all prepared according to literature procedures. Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F₂₅₄ 0.2 mm thickness precoated TLC plates, while column chromatography was performed using Merck Kieselgel 60 (0.040–0.063 mm, 230–400 mesh AST0000M).

General methods. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded at room temperature on a Bruker AVANCE III spectrometer at 400 MHz, 100 MHz, 376, and 162 MHz, respectively using residual solvent as the internal standard. All chemical shifts are quoted on the δ scale and coupling constants (*J*) are expressed in Hertz (Hz). The following abbreviations are used in listing the NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, and m = multiplet. Samples were prepared using CD₃SOCD₃ or CD₃COCD₃ purchased from Cambridge Isotope Labs. Electron Impact (EI) mass spectra were obtained on a Finnegan MAT TSQ 700 Triple Stage Quadrupole mass spectrometer, while matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a Bruker Autoflex III smartbeam Mass Spectrometer. Ultraviolet–visible–NIR (UV–vis–NIR) measurements were carried out in MeCN at 298 K on a Shimadzu UV-1601PC spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia.

MPTTF derivative 2. 2-{4-(2-(2-Methoxyethoxy)-ethylthio)-5-ethylthio-1,3-dithiol-2-ylidene}-(1,3)-dithiolo[4,5-*c*]pyrrole (275 mg, 0.63 mmol) was dissolved in anhydrous DMF (35 mL) and degassed (N₂, 15 min) before NaH (174 mg of a 55% suspension in mineral oil, 3.99 mmol) was added in one portion causing the initially yellow solution to become dark red. Subsequently, iodomethane (0.60 mL, 1.4 g, 9.6 mmol) was added in one portion and the reaction mixture immediately changed color to yellow. The reaction mixture was then stirred for 1.5 h at room temperature before being purged with N₂ (30 min). Thereafter, a saturated aqueous solution of NaCl (200 mL) was added to the reaction mixture, whereupon it was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (4 × 75 mL), H₂O (2 × 100 mL), dried (MgSO₄), and finally concentrated. The resulting yellow oil was purified by column chromatography (200 mL SiO₂, 2 cm Ø, CH₂Cl₂/EtOAc 10:1). The yellow band (*R*_f = 0.6) was collected and concentrated, providing the title compound **2** (251 mg, 85%) as a yellow brown oil. ¹H NMR (CD₃SOCD₃, 400 MHz) δ 1.24 (t, *J* = 7.2 Hz, 3H, CH₃CH₂S), 2.88 (q, *J* = 7.2 Hz, 2H, CH₃CH₂S), 3.02 (t, *J* = 6.4 Hz, 2H, SCH₂CH₂O), 3.23 (s, 3H, CH₃O), 3.42–3.44 (m, 2H, OCH₂), 3.51–3.54 (m, 2H, OCH₂), 3.58 (t, *J* = 6.4 Hz, 2H, SCH₂CH₂O), 3.60 (s, 3H, CH₃N), 6.77 (s, 2H, pyrrol-*H*). ¹³C NMR (CD₃SOCD₃, 100 MHz) δ 14.9, 29.6, 34.9, 36.8, 58.0, 69.1, 69.4, 71.1, 99.4, 107.2, 114.4 (two lines overlapping), 116.5, 120.9, 126.4, 126.9. MS (EI) *m/z* 451 (*M*⁺, 60), 199 (70), 155 (65), 59 (65), 44 (100), 42 (100). Anal. Calcd for C₁₆H₂₁NO₂S₆: C, 42.54; H, 4.69; N, 3.10; S, 42.59. Found: C, 42.83; H, 4.75; N, 3.19; S, 42.39.

Cyclobis(paraquat-*p*-phenylene) tetrakis(tris(tetrachlorobenzenediolato)phosphate(v))

CBPQT•4TRISPHAT. A solution of CBPQT•4PF₆ (26.0 mg, 0.024 mmol) in MeCN (2 mL) and a solution of morpholinium•TRISPHAT (111.2 mg, 0.130 mmol) in MeCN (3.5 mL) were mixed at

room temperature, whereupon the reaction mixture was evaporated to half the volume. Addition of cold ($\sim 0^\circ\text{C}$) MeOH (10 mL) gave a precipitate which was collected by filtration affording CBPQT•4TRISPHAT as a pale brown solid (67.5 mg, 80%). Mp. $>250^\circ\text{C}$. ^1H NMR (CD_3COCD_3 , 400 MHz) δ 6.20 (s, 8H, $4 \times \text{NCH}_2$), 7.93 (s, 8H, $8 \times \text{xylyl-H}$), 8.72 (d, $J=6.4$ Hz, 8H, $8 \times \beta\text{-H}$), 9.63 (d, $J=6.4$ Hz, 8H, $8 \times \alpha\text{-H}$). ^{31}P NMR (CD_3COCD_3 , 162 MHz) δ -80.6 . MS (MALDI) m/z 1288.6 ($[M - 3\text{TRISPHAT}]^+$, 15), 520.2 ($[M - 4\text{TRISPHAT}]^+$, 100). Anal. Calcd for $\text{C}_{108}\text{H}_{32}\text{Cl}_{48}\text{N}_4\text{O}_{24}\text{P}_4 \cdot 2\text{H}_2\text{O}$: C, 35.72; H, 1.00; N, 1.54. Found: C, 35.49; H, 0.95; N, 1.68.

Crystals suitable for X-ray crystallography were grown by dissolving a 1:1 mixture of the MPTTF derivative 2 and CBPQT•4TRISPHAT in MeCN. Subsequently, a layer of petroleum ether was placed on top of the MeCN solution and the mixture was allowed to evaporate slowly, affording brown crystals of CBPQT•4TRISPHAT.

Crystal data were collected on a Bruker APEX-II CCD. Crystal data for CBPQT•4TRISPHAT•6CH₃CN: $\text{C}_{120}\text{H}_{50}\text{Cl}_{48}\text{N}_{10}\text{O}_{24}\text{P}_4$, $M = 3841.18$, triclinic, $a = 14.821(4)$, $b = 15.650(5)$, $c = 17.686(5)$ Å, $\alpha = 74.787(4)$, $\beta = 87.859(4)$, $\gamma = 66.476(4)^\circ$, $V = 3618.9(18)$ Å³, $T = 296(2)$ K, space group $P-1$, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 1.011$ mm⁻¹, 20594 reflections measured, 16007 unique ($R_{\text{int}} = 0.0275$), $R1[I > 2\sigma(I)] = 0.1045$, $wR2(\text{all data}) = 0.2347$.

NMR spectroscopic characterisation of CBPQT•4TRISPHAT

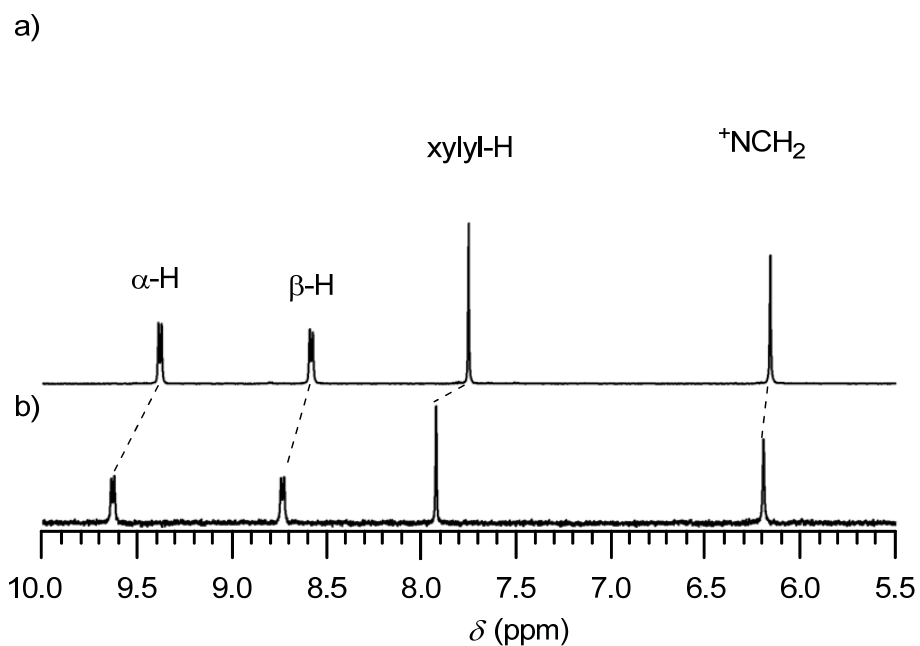


Fig. S1 Partial ¹H NMR spectra (400 MHz, 298 K) recorded in CD₃COCD₃ of a) CBPQT•4PF₆ and b) CBPQT•4TRISPHAT.

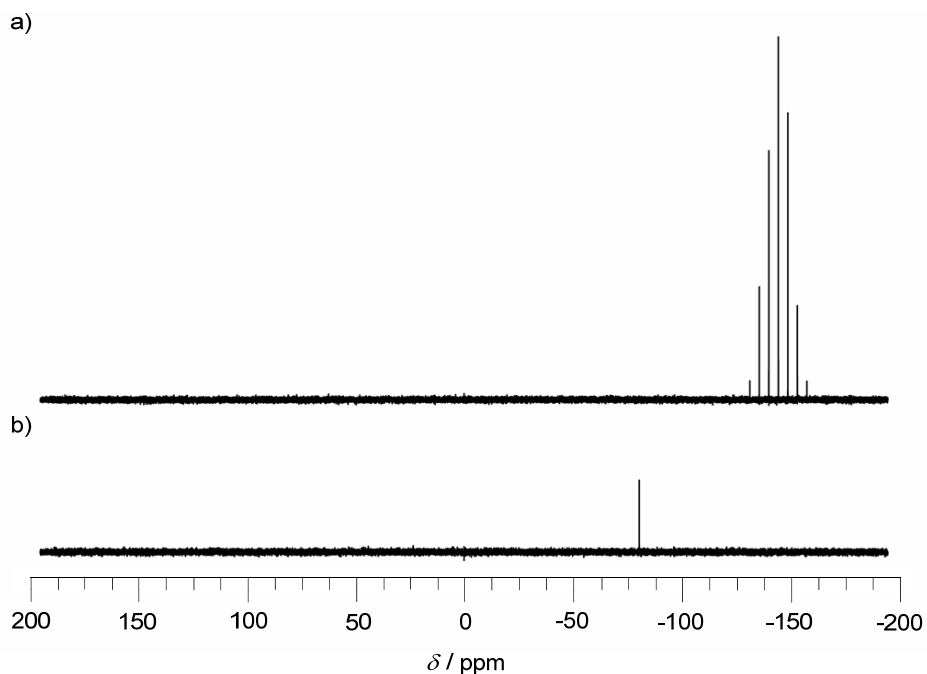


Fig. S2 ³¹P NMR spectra (162 MHz, 298 K) recorded in CD₃COCD₃ of a) CBPQT•4PF₆ and b) CBPQT•4TRISPHAT.

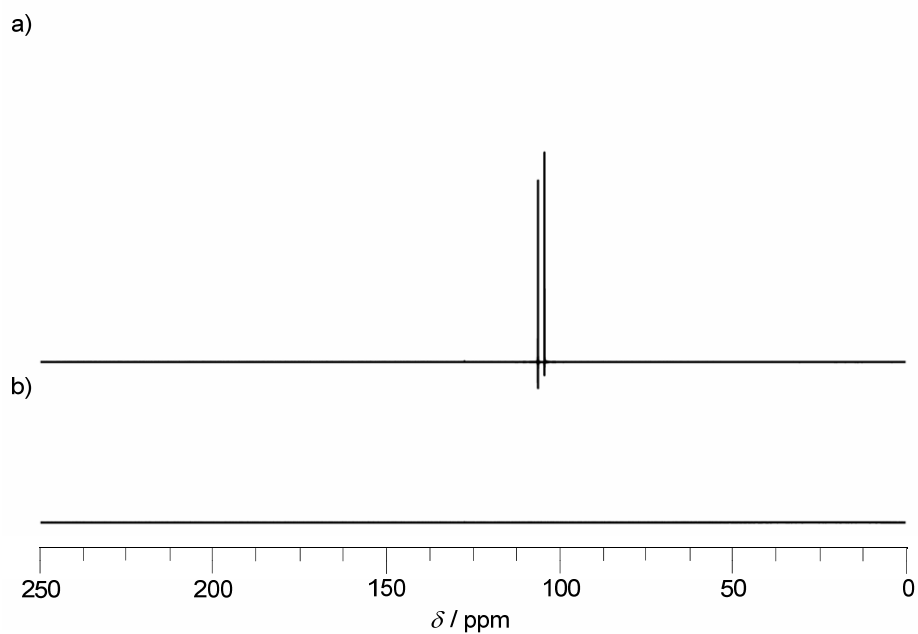


Fig. S3 ^{19}F NMR spectra (376 MHz, 298 K) recorded in CD_3COCD_3 of a) $\text{CBPQT}\cdot 4\text{PF}_6$ and b) $\text{CBPQT}\cdot 4\text{TRISPHAT}$.

Example of determination of binding constant (K_a) between CBPQT•4PF₆ and the MPTTF derivative **2**

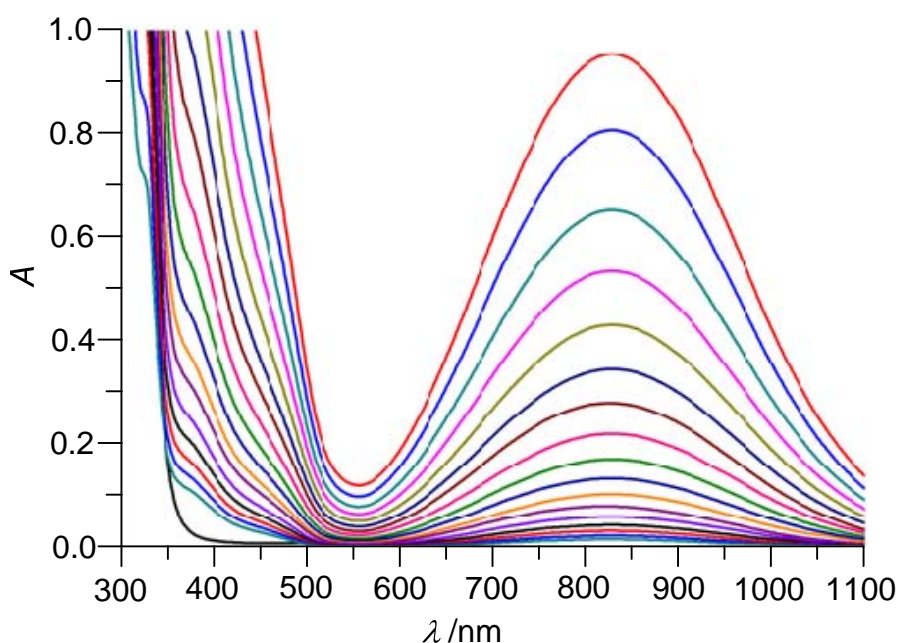


Fig. S4 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆. The first spectrum was recorded with $[2] = [\text{CBPQT}^{4+}] = 9.0 \times 10^{-4}$ M and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of 4.1×10^{-5} M.

Mixing the colorless cyclophane CBPQT•4PF₆ and the MPTTF derivative **2** in equimolar proportions in MeCN immediately produced a green-colored solution, as a result of the appearance of a charge transfer (CT) absorption band, centered around $\lambda_{\text{max}} = 830$ nm (Fig. S4). A starting solution (3 mL) with a absolute concentration (c) of 9.0×10^{-4} M was placed in the thermostatted cell compartment of the UV-vis spectrophotometer and allowed to equilibrate at 298 K, before the absorbance A was measured at 830 nm (λ_{max}). Subsequently, the solution was repeatedly diluted (a sixth part each time) with MeCN, down to a final absolute concentration of 4.1×10^{-5} M. After each dilution, the solution was allowed to equilibrate at 298 K before the absorbance A was measured at 830 nm (λ_{max}), which resulted (Table S1) in 18 data points $[1/A^{1/2}, c/A]$ for **2**•CBPQT•4PF₆.

UV-vis dilution experiment for the complexation of the MPTTF derivative **2** and CBPQT•4PF₆ in MeCN at 298 K

Optical path length: $l = 1$ cm
 CBPQT•PF₆ in MeCN $\varepsilon = 25 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830$ nm
2 in MeCN $\varepsilon = 4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830$ nm
 Total “background” (A_b) $\varepsilon = 29 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830$ nm

Table S1 The absorbance A_m for 1:1 mixture of CBPQT•4PF₆ and **2** in MeCN was measured at $\lambda_{\text{max}} = 830$ nm at different concentrations c and subtracted the “background absorbance” (at $\lambda_{\text{max}} = 830$ nm) equal to $A_b = 29 \text{ M}^{-1} \times c$ giving $A = A_m - A_b = A_m - 29 \text{ M}^{-1} \times c$.

c (M)	A_m	A	$1/A^{1/2}$	c/A (M)
0.000900	0.9550	0.9287	1.0377	0.000969
0.000750	0.8086	0.7867	1.1275	0.000953
0.000625	0.6547	0.6364	1.2535	0.000982
0.000521	0.5381	0.5229	1.3829	0.000996
0.000434	0.4348	0.4221	1.5392	0.001028
0.000362	0.3495	0.3389	1.7177	0.001067
0.000301	0.2841	0.2753	1.9059	0.001095
0.000251	0.2253	0.2180	2.1420	0.001152
0.000209	0.1764	0.1703	2.4233	0.001229
0.000174	0.1394	0.1343	2.7287	0.001299
0.000145	0.1091	0.1049	3.0882	0.001386
0.000121	0.0859	0.0824	3.4845	0.001471
0.000101	0.0659	0.0630	3.9857	0.001604
0.000084	0.0497	0.0472	4.6008	0.001781
0.000070	0.0387	0.0367	5.2234	0.001912
0.000058	0.0298	0.0281	5.9662	0.002079
0.000049	0.0228	0.0213	6.8395	0.002277
0.000041	0.0178	0.0166	7.7581	0.002442

Plotting c/A against $1/A^{1/2}$ afforded a straight line with slope α of $(1/K_a \varepsilon l)^{1/2}$ and a y intercept y_0 of $1/\varepsilon l$, where ε is the molar extinction coefficient for the CT band of the complex and l is the optical path length.^{S6} The linear relationship (Fig. S5) between c/A and $1/A^{1/2}$ was demonstrated by calculation of the correlation coefficient and a value of 0.9979 was obtained. The K_a and ε (Table S2) values were obtained from the relationship^{S6} $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\varepsilon l$ is the slope and y -intercept of the line, respectively. The free energies of complexation (ΔG° , Table S2)

where calculated using the relationship $\Delta G^0 = -RT\ln K_a$, where R is the gas constant and T is the absolute temperature.

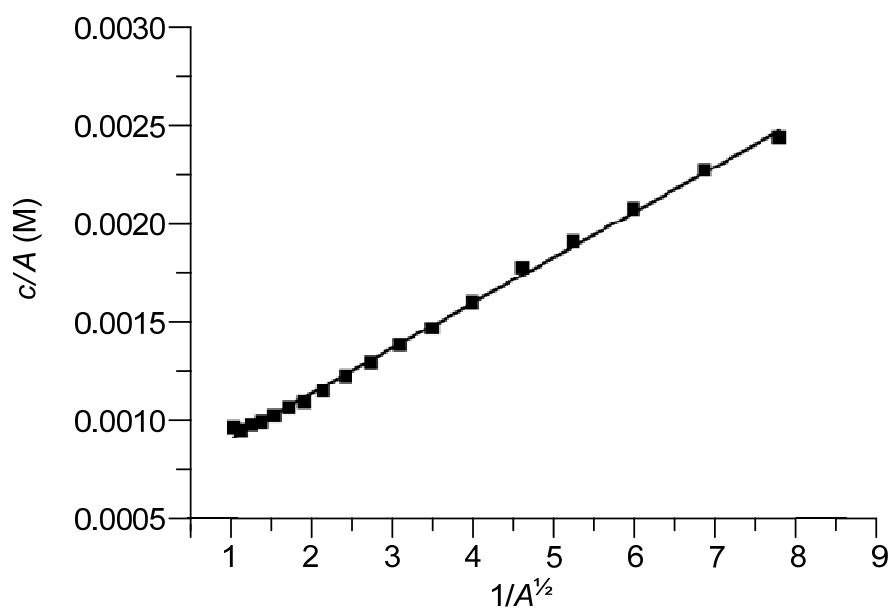


Fig. S5 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆. The absorbance A was measured at several different absolute concentrations (c).

The binding constant between the MPTTF derivative **2** and CBPQT•4TRISPHAT was determined using an similar method and so was the binding constants between the electron donors **1**, **3** and **4** and CBPQT•4PF₆ and CBPQT•4TRISPHAT. The absorption spectra and the linear plots (c/A against $1/A^{1/2}$) for each measurement are show below.

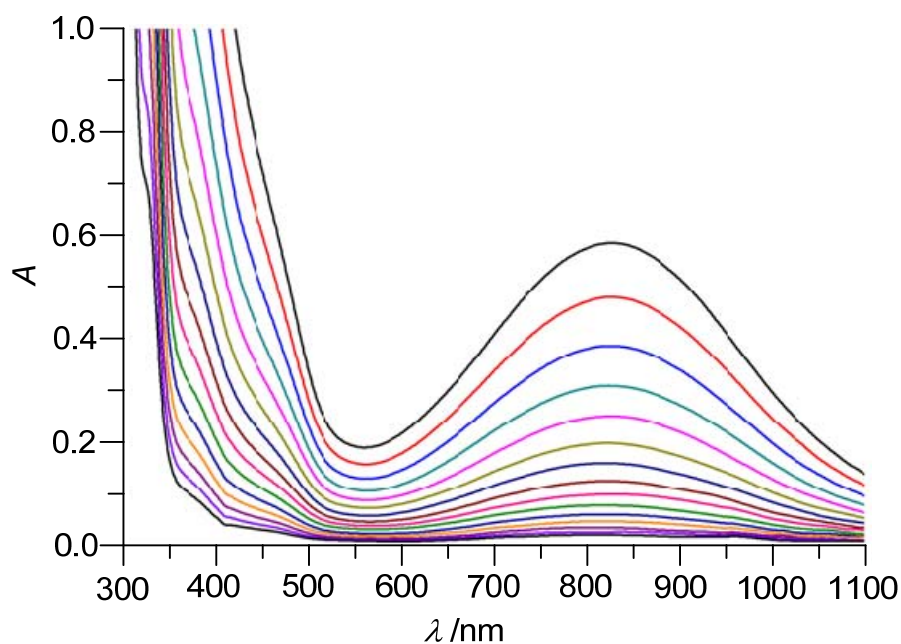


Fig. S6 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of the MPTTF derivative **2** and CBPQT•4TRISPHAT. The first spectrum was recorded with $[2] = [\text{CBPQT}^{4+}] = 5.0 \times 10^{-4} \text{ M}$ and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of $3.9 \times 10^{-5} \text{ M}$.

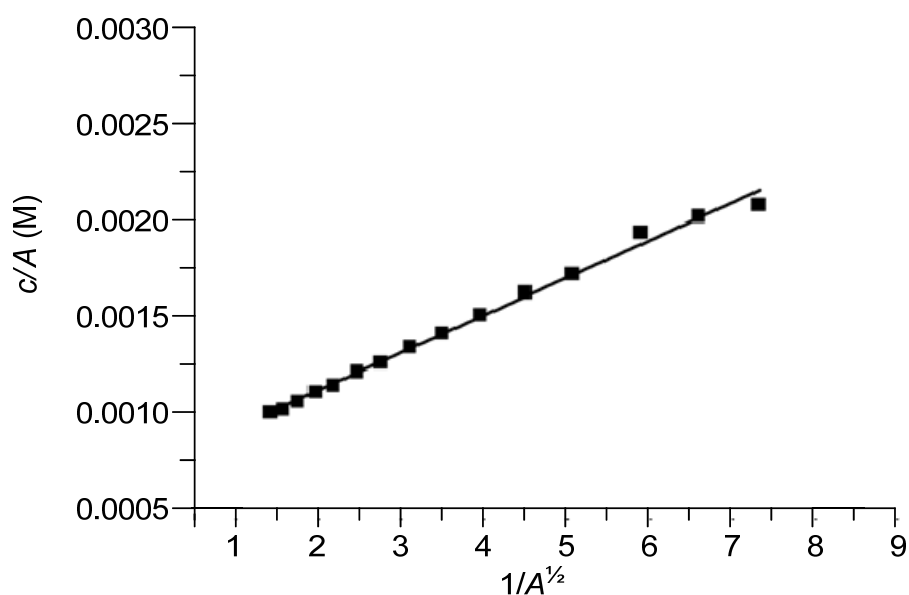


Fig. S7 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the MPTTF derivative **2** and CBPQT•4TRISPHAT. The absorbance A was measured at several different absolute concentrations (c).

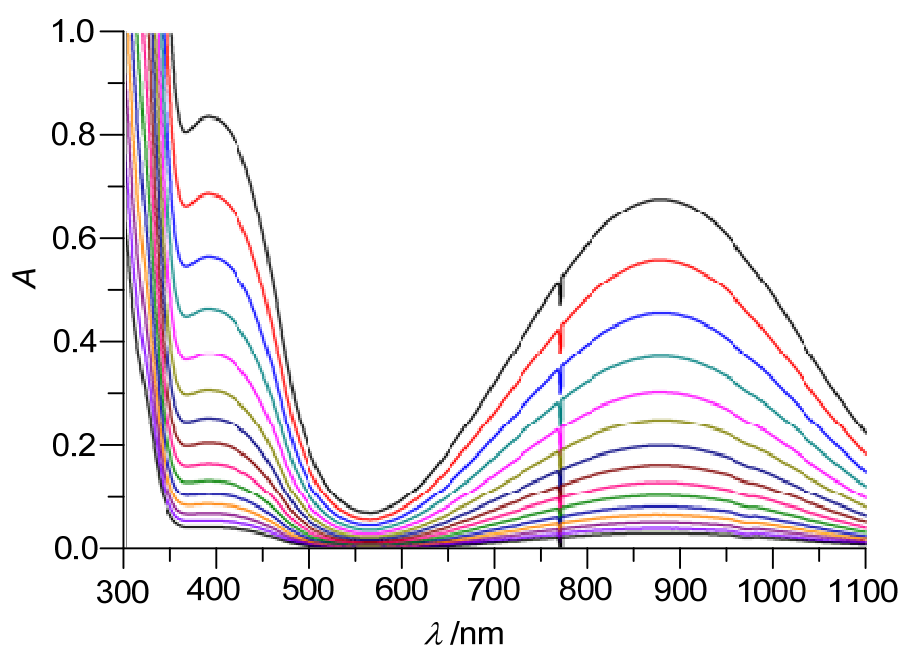


Fig. S8 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of the BPTTF derivative **3** and CBPQT•4PF₆. The first spectrum was recorded with $[3] = [\text{CBPQT}^{4+}] = 4.0 \times 10^{-4} \text{ M}$ and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of $3.1 \times 10^{-5} \text{ M}$.

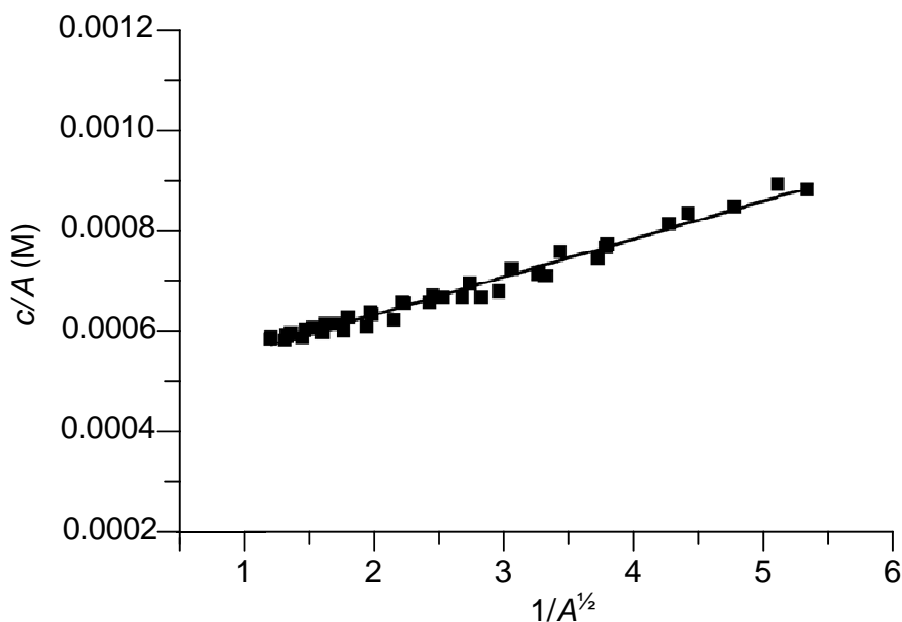


Fig. S9 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the BPTTF derivative **3** and CBPQT•4PF₆. The absorbance A was measured at several different absolute concentrations (c).

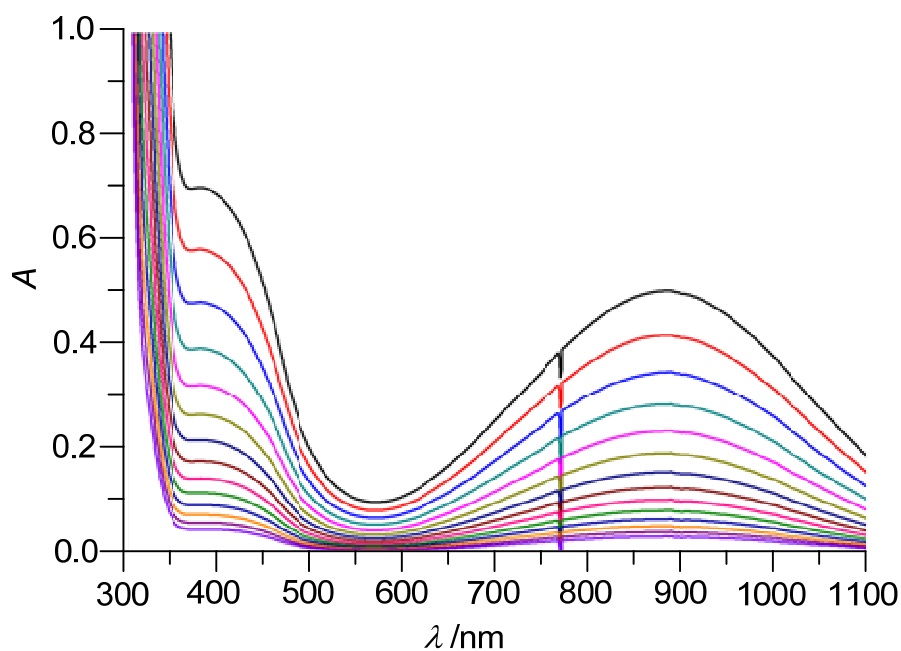


Fig. S10 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of the BPTTF derivative **3** and CBPQT•4TRISPHAT. The first spectrum was recorded with $[3] = [CBPQT^{4+}] = 3.0 \times 10^{-4}$ M and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of 2.8×10^{-5} M.

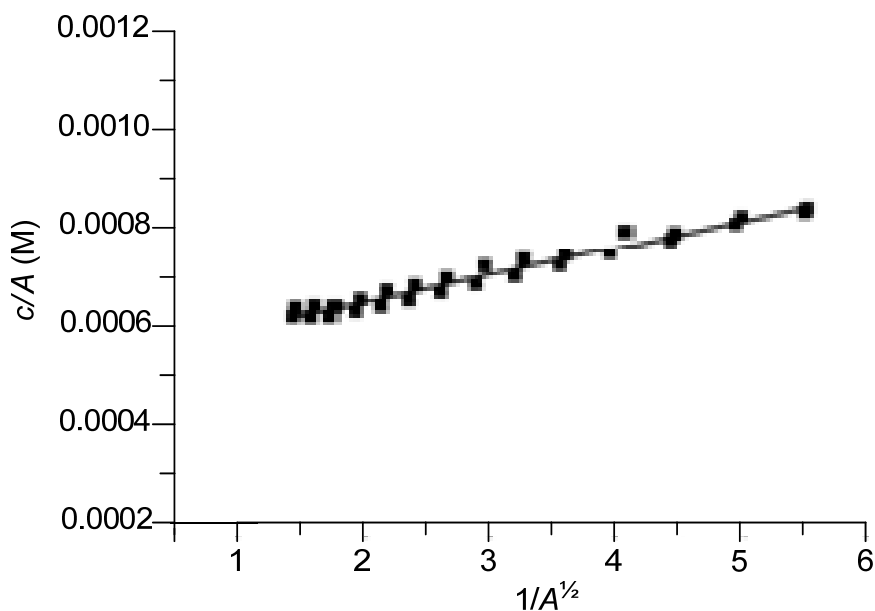


Fig. S11 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the BPTTF derivative **3** and CBPQT•4THRISPHAT. The absorbance A was measured at several different absolute concentrations (c).

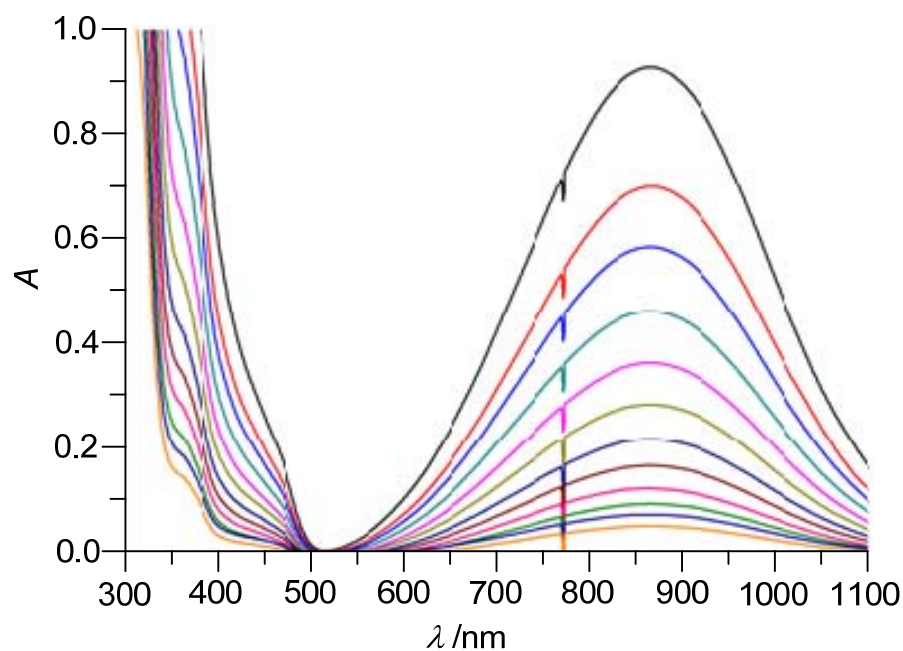


Fig. S12 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of TTF **1** and CBPQT•4PF₆. The first spectrum was recorded with $[1] = [\text{CBPQT}^{4+}] = 4.8 \times 10^{-4} \text{ M}$ and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of $5.4 \times 10^{-5} \text{ M}$.

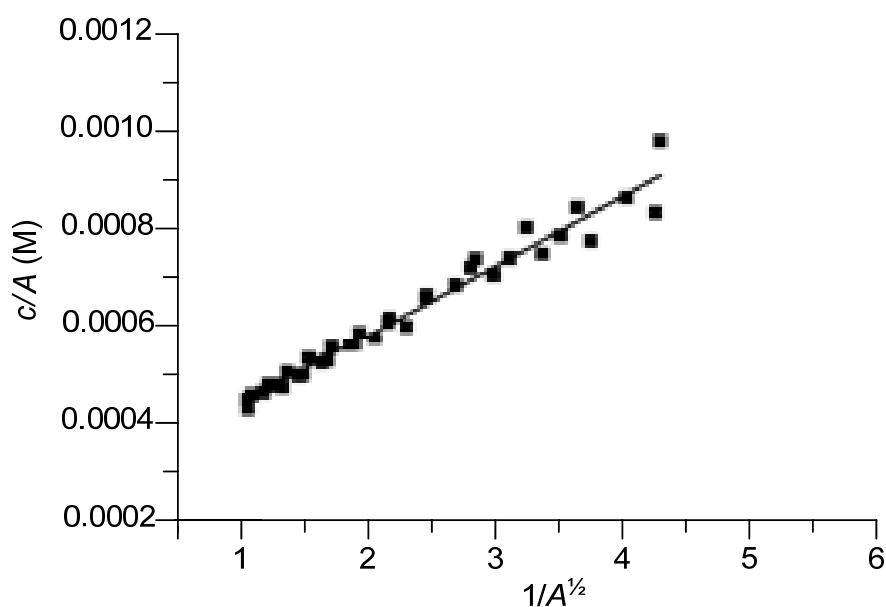


Fig. S13 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of TTF **1** and CBPQT•4PF₆. The absorbance A was measured at several different absolute concentrations (c).

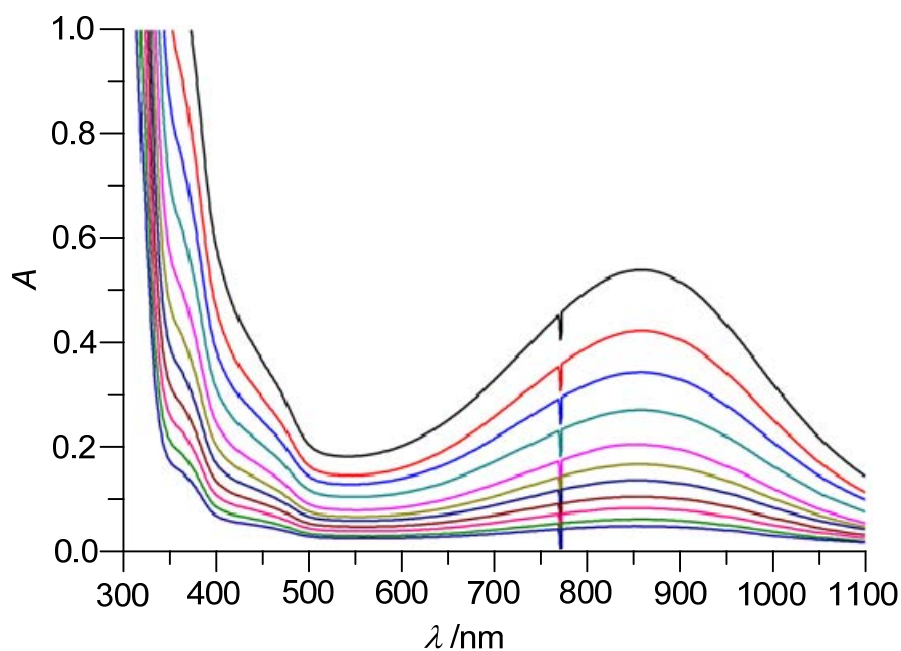


Fig. S14 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of TTF **1** and CBPQT•4TRISPHAT. The first spectrum was recorded with $[1] = [\text{CBPQT}^{4+}] = 2.7 \times 10^{-4} \text{ M}$ and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of $4.3 \times 10^{-5} \text{ M}$.

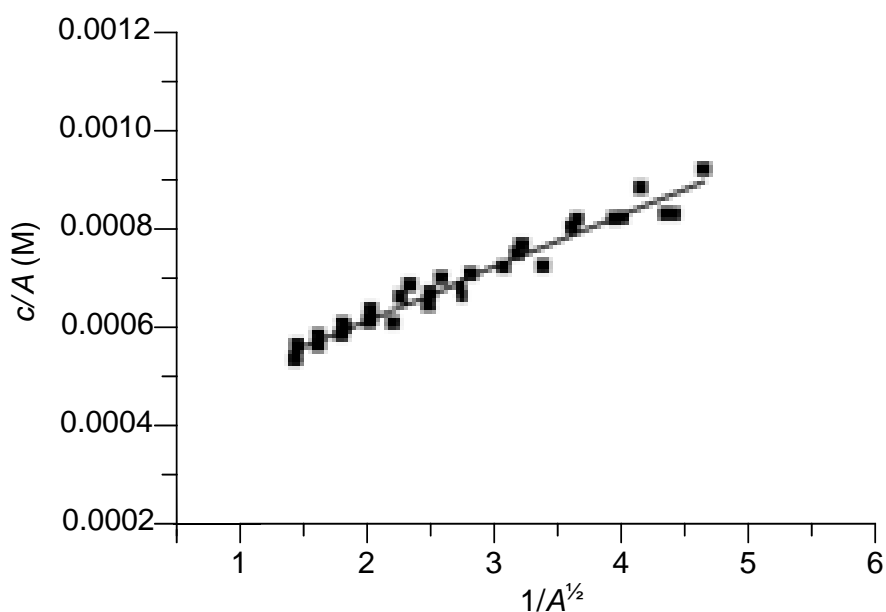


Fig. S15 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of TTF **1** and CBPQT•4TRISPHAT. The absorbance A was measured at several different absolute concentrations (c).

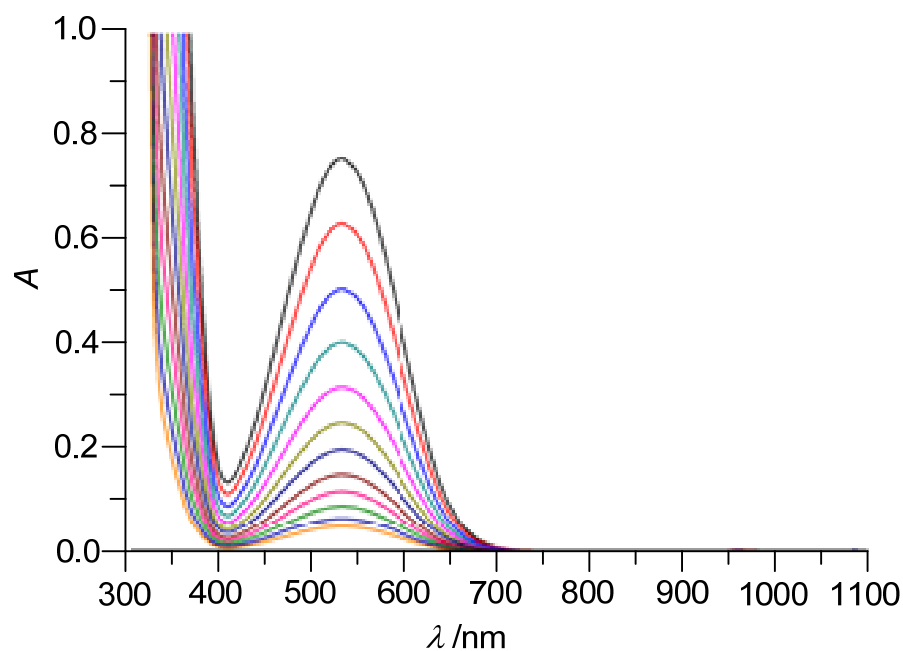


Fig. S16 Absorption spectra recorded in MeCN at 298 K of a 1:1 mixture of the DNP derivative **4** and CBPQT•4PF₆. The first spectrum was recorded with [4] = [CBPQT⁴⁺] = 1.8×10^{-3} M and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN, down to a final absolute concentration of 2.4×10^{-4} M.

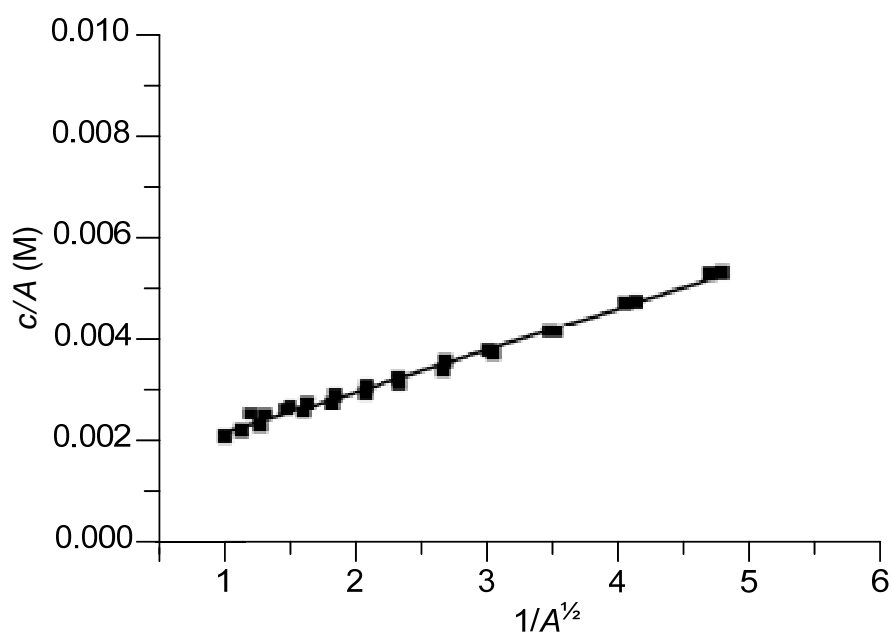


Fig. S17 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the DNP derivative **4** and CBPQT•4PF₆. The absorbance A was measured at several different absolute concentrations (c).

Table S2 Comparison of binding constants (K_a values) and derived free energies of complexation (ΔG°) between the electron donors **1–4** and CBPQT•4PF₆ or CBPQT•4TRISPHAT determined by absorption spectroscopy at 298 K in MeCN using the TTF/CBPQT⁴⁺ or DNP/CBPQT⁴⁺ CT band as probes

	λ_{max} (nm)	Data points	R^2	ε (L mol ⁻¹ cm ⁻¹) ^a	K_a (M ⁻¹) ^a	ΔG° (kcal mol ⁻¹) ^a
1 ⊂CBPQT•4PF ₆	860	37	0.9698	3300 ± 500	15000 ± 2300	-5.70 ± 0.09
1 ⊂CBPQT•4TRISPHAT	860	33	0.9595	2400 ± 400	37000 ± 6200	-6.23 ± 0.10
2 ⊂CBPQT•4PF ₆	830	18	0.9979	1500 ± 200	13000 ± 900	-5.61 ± 0.04
2 ⊂CBPQT•4TRISPHAT	830	15	0.9943	1400 ± 100	20000 ± 900	-5.87 ± 0.03
3 ⊂CBPQT•4PF ₆	880	33	0.9769	2100 ± 100	84000 ± 3000	-6.72 ± 0.03
3 ⊂CBPQT•4TRISPHAT	880	28	0.9683	1800 ± 100	176000 ± 12000	-7.16 ± 0.05
4 ⊂CBPQT•4PF ₆	530	25	0.9906	750 ± 100	2000 ± 100	-4.50 ± 0.04

^a The errors are determined according to literature procedure^{S6} using $\Delta T = 1$, $\Delta c = 0.03$ and $\Delta A = 0.01$.

Example of determination of binding constant (K_a) between CBPQT•4PF₆ and the MPTTF derivative **2 in the presence of 0.1 M *n*-Bu₄N•ClO₄**

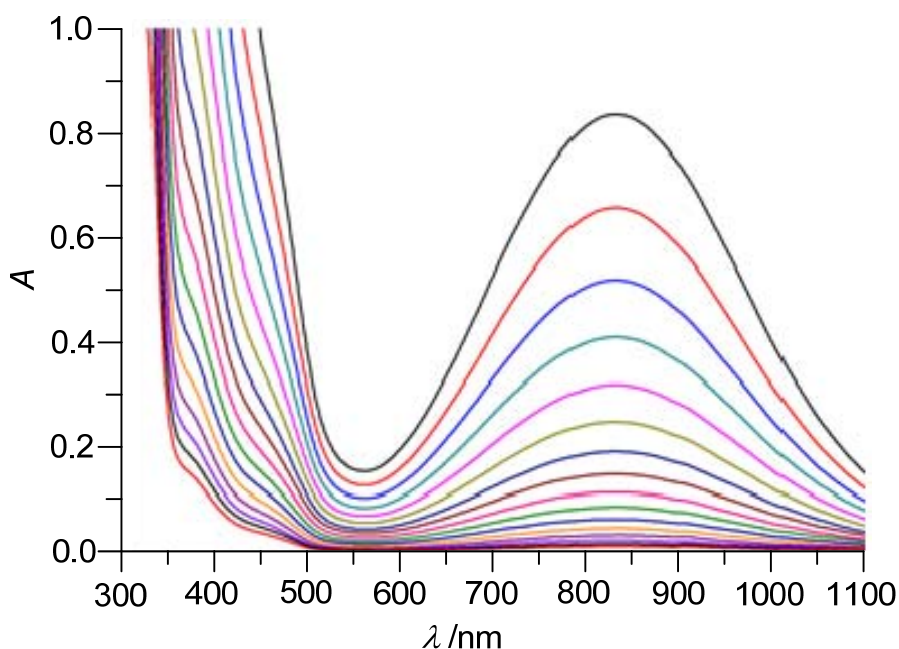


Fig. S18 Absorption spectra recorded in MeCN containing 0.1 M *n*-Bu₄N•ClO₄ at 298 K of a 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆. The first spectrum was recorded with $[2] = [CBPQT^{4+}] = 9.0 \times 10^{-4}$ M and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN containing 0.1 M *n*-Bu₄N•ClO₄, down to a final absolute concentration of 5.8×10^{-5} M.

Mixing the colorless cyclophane CBPQT•4PF₆ and the MPTTF derivative **2** in equimolar proportions in MeCN containing 0.1 M *n*-Bu₄N•ClO₄ immediately produced a green-colored solution, as a result of the appearance of a CT absorption band, centered around $\lambda_{\text{max}} = 830$ nm (Fig. S18). A starting solution (3 mL) with a absolute concentration (c) of 9.0×10^{-4} M was placed in the thermostatted cell compartment of the UV-vis spectrophotometer and allowed to equilibrate at 298 K, before the absorbance A was measured at 830 nm (λ_{max}). Subsequently, the solution was repeatedly diluted (a sixth part each time) with MeCN containing 0.1 M *n*-Bu₄N•ClO₄, down to a final absolute concentration of 5.8×10^{-5} M. After each dilution, the solution was allowed to equilibrate at 298 K before the absorbance A was measured at 830 nm (λ_{max}), which resulted (Table S3) in 16 data points $[1/A^{1/2}, c/A]$ for **2**•CBPQT•4ClO₄.

UV-vis dilution experiment for the complexation of the MPTTF derivative **2 and CBPQT⁴⁺ in MeCN containing 0.1 M *n*-Bu₄N•ClO₄ at 298 K.**

Optical path length:	$l = 1 \text{ cm}$
CBPQT•PF ₆ in MeCN	$\varepsilon = 25 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830 \text{ nm}$
2 in MeCN	$\varepsilon = 4 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830 \text{ nm}$
Total “background” (A_b)	$\varepsilon = 29 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 830 \text{ nm}$

Table S3 The absorbance A_m for 1:1 mixture of CBPQT•4PF₆ and **2** in MeCN containing 0.1 M *n*-Bu₄N•ClO₄ was measured at $\lambda_{\text{max}} = 830 \text{ nm}$ at different concentrations c and subtracted the “background absorbance” (at $\lambda_{\text{max}} = 830 \text{ nm}$) equal to $A_b = 29 \text{ M}^{-1} \times c$ giving $A = A_m - A_b = A_m - 29 \text{ M}^{-1} \times c$.

$c \text{ (M)}$	A	A_m	$1/(A^{1/2})$	$c/A \text{ (M)}$
0.000900	0.8374	0.8111	1.1104	0.001110
0.000750	0.6606	0.6387	1.2513	0.001174
0.000625	0.5234	0.5051	1.4070	0.001237
0.000521	0.4143	0.3991	1.5830	0.001305
0.000434	0.3235	0.3108	1.7937	0.001396
0.000362	0.2529	0.2423	2.0314	0.001493
0.000301	0.1962	0.1874	2.3101	0.001608
0.000251	0.1532	0.1459	2.6184	0.001722
0.000209	0.1187	0.1126	2.9803	0.001859
0.000174	0.0909	0.0858	3.4139	0.002033
0.000145	0.0676	0.0634	3.9730	0.002294
0.000121	0.0508	0.0473	4.5999	0.002563
0.000101	0.0377	0.0348	5.3644	0.002905
0.000084	0.0281	0.0256	6.2449	0.003280
0.000070	0.0210	0.0190	7.2640	0.003699
0.000058	0.0160	0.0142	8.3645	0.004087

Plotting c/A against $1/A^{1/2}$ afforded a straight line with slope α of $(1/K_a \varepsilon l)^{1/2}$ and a y intercept y_0 of $1/\varepsilon l$, where ε is the molar extinction coefficient for the CT band of the complex and l is the optical path length.^{S6} The linear relationship (Fig. S19) between c/A and $1/A^{1/2}$ was demonstrated by calculation of the correlation coefficient and a value of 0.9995 was obtained. The K_a and ε values (Table S4) were obtained from the relationship^{S6} $K_a = y_0/\alpha^2$, where α and $y_0 = 1/\varepsilon l$ is the slope and y -intercept of the line, respectively. The free energies of complexation (ΔG^0 , Table S4) were calculated using the relationship $\Delta G^0 = -RT \ln K_a$, where R is the gas constant and T is the absolute temperature.

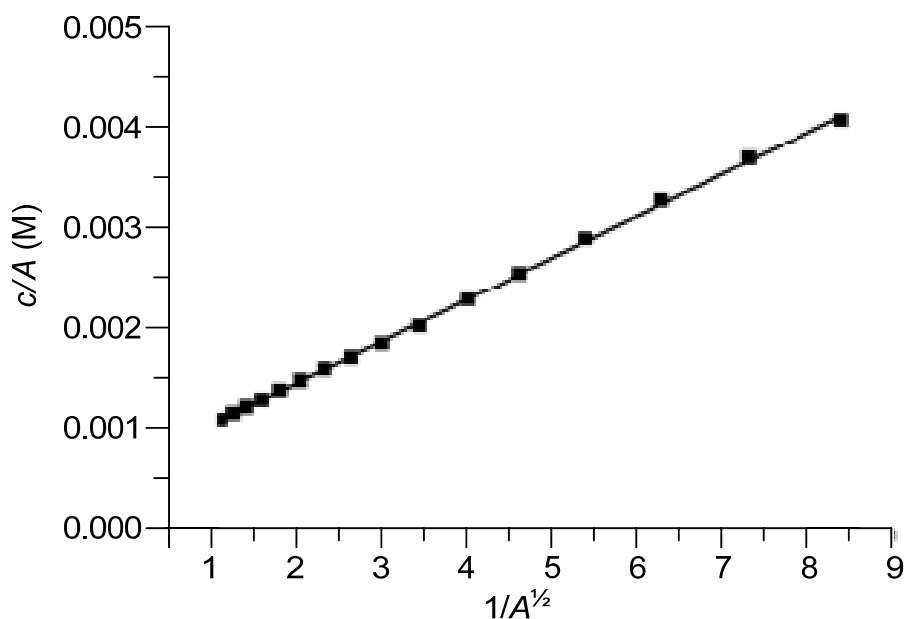


Fig. S19 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆ in MeCN containing 0.1 M *n*-Bu₄N•ClO₄. The absorbance A was measured at several different absolute concentrations (c).

The binding constant between the MPTTF derivative **2** and CBPQT•4PF₆ in the presence of 0.1 M *n*-Bu₄N•PF₆ was determined using an identical approach, with a starting solution having an absolute concentration c of 9.0×10^{-4} M. The starting solution was subsequently repeatedly diluted to a final absolute concentration c of 4.9×10^{-5} M. In these experiment, the CT absorption band was centered around $\lambda_{\text{max}} = 830$ nm (Fig. S20) and a total of 16 data point were obtained.

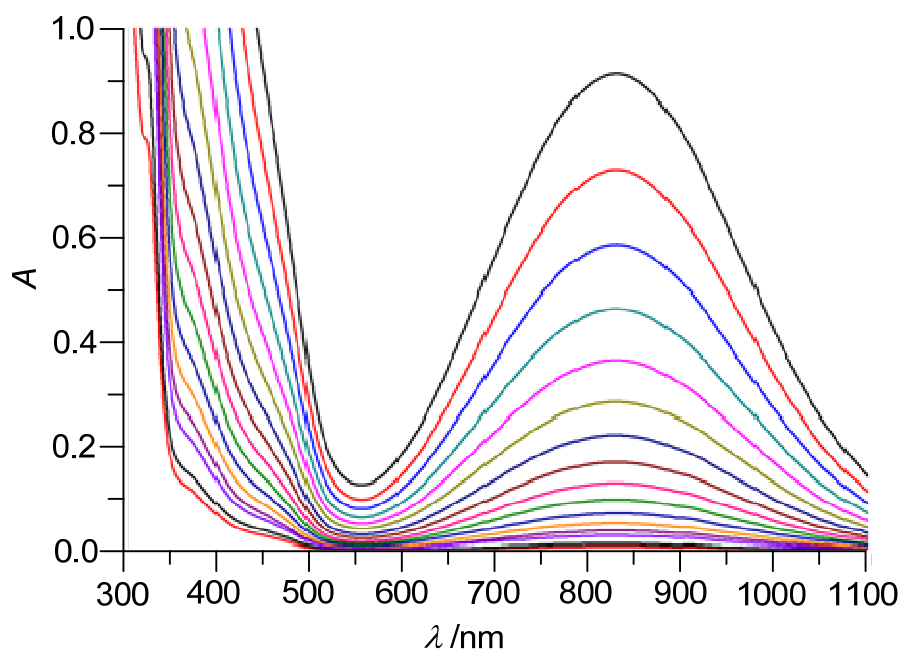


Fig. S20 Absorption spectra recorded in MeCN containing 0.1 M *n*-Bu₄N•PF₆ at 298 K of a 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆. The first spectrum was recorded with [2] = [CBPQT⁴⁺] = 9.0×10^{-4} M and the subsequent spectra were obtained from solutions diluted a sixth part each time with MeCN containing 0.1 M *n*-Bu₄N•PF₆, down to a final absolute concentration of 4.9×10^{-5} M.

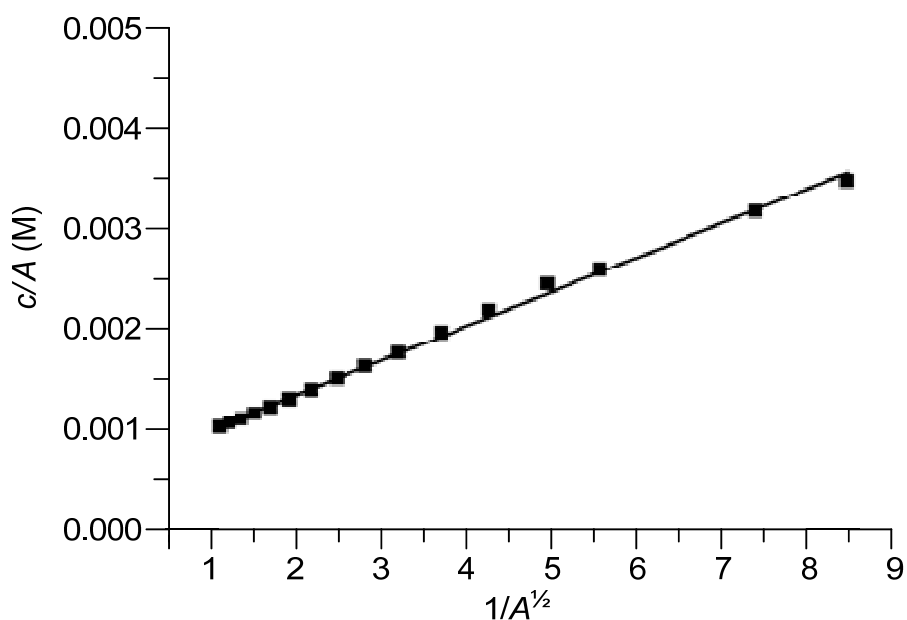


Fig. S21 Linear plot of c/A against $1/A^{1/2}$ for 1:1 mixture of the MPTTF derivative **2** and CBPQT•4PF₆ in MeCN containing 0.1 M *n*-Bu₄N•PF₆. The absorbance A was measured at several different absolute concentrations (c).

Table S4 Comparison of binding constants (K_a values) and derived free energies of complexation (ΔG°) between the MPTTF derivative **2** and CBPQT•4TRISPHAT, CBPQT•4PF₆, CBPQT•4PF₆ + 0.1 M *n*-Bu₄N•PF₆ and CBPQT•4PF₆ + 0.1 M *n*-Bu₄N•ClO₄ determined by absorption spectroscopy at 298 K in MeCN using the MPTTF/CBPQT⁴⁺ CT band as probe

	λ_{\max} (nm)	Data points	R^2	E (L mol ⁻¹ cm ⁻¹) ^a	K_a (M ⁻¹) ^a	ΔG° (kcal mol ⁻¹) ^a
CBPQT•4TRISPHAT	830	15	0.9943	1400 ± 200	20000 ± 2000	-5.85 ± 0.06
CBPQT•4PF ₆	830	18	0.9979	1500 ± 300	13000 ± 2000	-5.60 ± 0.07
CBPQT•4PF ₆ + 0.1 M <i>n</i> -Bu ₄ N•PF ₆	830	16	0.9972	1500 ± 100	5600 ± 100	-5.11 ± 0.02
CBPQT•4PF ₆ + 0.1 M <i>n</i> -Bu ₄ N•ClO ₄	830	16	0.9995	1600 ± 200	3700 ± 100	-4.87 ± 0.02

^a The errors are determined according to literature procedure^{S6} using $\Delta T = 1$, $\Delta c = 0.03$ and $\Delta A = 0.01$

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